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PRELIMINARY STUDY OF FORESTRY HERBICIDE RESIDUES IN NORTHERN NEW BRUNSWICK

IWD-AR-WQB-85-83

INLAND WATERS DIRECTORATE
ATLANTIC REGION
WATER QUALITY BRANCH
MONCTON, NEW BRUNSWICK

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Inland Waters Directorate

Environment Canada

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A copy will be made available in French upon request

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ABSTRACT

A marshy pond located in a Northern New Brunswick study area was treated with a phenoxy herbicide, the isooctyl ester of 2,4,5-T. The concentrations measured in pond water samples over time suggested that the 2,4,5-T isooctyl ester underwent hydrolysis to form the corresponding phenoxy acid. Other degradation processes likely influenced the persistence of the isooctyl ester and corresponding acid (2,4,5-T) in this aquatic milieu. The hydrological dynamics of the pond dissipated the two products with time. The herbicide concentrations measured in bottom sediment samples demonstrated a diminishing trend with time.

A parallel study was performed to determine the levels of polychlorinated dibenzo-p-dioxins and dibenzofurans present in the technical product and in environmental samples collected at the study site. The results are presented in this report.

RÉSUMÉ

Un marais situé dans une région d'étude au Nord du Nouveau-Brunswick fut traité par un phénoxy herbicide, l'ester isooctyle du 2,4,5-T. A la lumière des concentrations détectées dans les échantillons d'eau recueillis dans le marais, il semble que l'ester isooctyle du 2,4,5-T s'est hydrolysée avec le temps pour former le phénoxy acide correspondant. D'autres processus dégradatifs influencèrent probablement la persistance de l'ester isooctyle et de l'acide correspondant (2,4,5-T) dans ce milieu aquatique. La dynamique hydrologique du marais a dispersé les deux substances avec le temps. Les concentrations d'herbicide mesurées dans les échantillons de sédiments de fond demontrèrent une tendance vers la diminution avec le temps.

Une étude parallèle a été conduite pour évaluer la présence de dibenzo-p-dioxines et dibenzofurannes polychlorés dans le produit technique et dans des échantillons environnementaux prélevés du site étudié. Les résultats obtenus sont présentés.

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1. INTRODUCTION

The use of herbicides in forestry is an issue which has received a considerable amount of public attention within the Atlantic Region. Central to the controversy is the fact that there is some disagreement within the scientific community regarding the magnitude of associated human health and environmental effects which accompany the use patterns. Of particular concern to the public and regulators alike is the fact that there have been very few regional investigations to determine the fate and effects of phenoxy herbicides used for forestry purposes.

The New Brunswick Department of Natural Resources (DNR) conducts a conifer release program in certain areas of the province as an integral part of its effort to replant clear cut forest areas. Two to four years after planting the seedlings, herbicide is applied to these replanted sites. This allows free growth of the conifers by killing or retarding the growth of particular competing deciduous species.

In co-operation with DNR, the Inland Waters Directorate (IWD) and Environmental Protection Service (EPS) of Environment Canada designed a project to look at the fate of a forestry herbicide in a regional context. The IWD component of this project was to measure the fate and persistence of the parent phenoxy herbicide, 2,4,5-T isooctyl ester and 2,4,5-T (2,4,5-trichlorophenoxy acetic acid), in a pond as a function of time after normal silvicultural dosage rates. EPS was to measure the concentrations of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) present in the technical product and in environmental samples collected at the study site.

In Canada phenoxy herbicides are used to control broad-leaved weeds, hardwood trees, and brush on crop and range land, in forests, on rights-of-way, on industrial property, on turf and on lawns. Most grass, coniferous, and some leguminous species are fairly resistant to these herbicides. In lakes, ponds and ditches, they are applied to kill rooted macrophytes as well as floating and submerged weeds. The various uses differ primarily in the quantities of herbicide applied and the mode and frequency of application required for control of unwanted plants. The most commonly used phenoxy herbicide in Canada is 2,4-D (National Research Council of Canada (NRCC), 1978).

Following their application, herbicides are dispersed to varying degrees by a number of processes. During and immediately after application, volatilization and drift may be major pathways of loss. The fraction intercepted and held by vegetation, soil, or water may then be transported by several routes within and between ecosystems. Before, during and after transport, various modes of degradation (chemical, photochemical, or micro biological) may act on the original formulation, changing its chemistry and toxicity (NRCC, 1978). In natural waters, the half life of 2,4-D can be short (one to several weeks) while 2,4,5-T may persist for about 5 weeks (Hebda and Jones, 1982). Temperature, oxygen concentration, pH, light intensity, types of micro-organisms present and organic content are factors affecting phenoxy herbicide loss from water (Norris, 1981). Herbicide concentrations disperse in moving water systems more quickly than they do in standing water due to transport from a particular site (NRCC, 1978).

The contamination of commercially available 2,4,5-T with polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has been of much concern in recent years since these chemicals were alleged to be involved in a number of serious incidents (Kimbrough, 1984; Rappe, 1984). There are a number of proposed and documented sources of dioxins, all of which involve unintentional production during chemical synthesis. Probably the most important known source of PCDDs and PCDFs is in the production of polychlorinated phenols and their derivatives, which include 2,4-D and 2,4,5-T (Esposito et al. 1980; Mitchell, 1984).

The presence of PCDDs and PCDFs in chlorophenoxy herbicides, notably 2,4,5-T, first received wide scale attention in the late 1960s when it was acknowldged that the military defoliant, known as Agent Orange, was contaminated with the 2,3,7,8-tetra isomer (Bovey and Young, 1980). While the concentration of 2,3,7,8-TCDD in the mixed butyl ester combination of 2,4-D and 2,4,5-T which was used in Vietnam ranged from 0.1 to 47 ug/g (Rappe, 1978a), commercially available 2,4,5-T may have been slightly less contaminated (Rappe et al., 1978). The same investigators also observed that this 2,4,5-T contained other PCDD and PCDF congeners in lower concentrations (0.02 to 0.50 ug/g). In Canada at present, the amount of 2,3,7,8-TCDD in commercially available 2,4,5-T may not exceed 0.1 ug/g (ppm), as specified by regulations under the Pest Control Products Act. The concentrations of other congeners is uncontrolled.

PCDDs and PCDFs are two groups of tricyclic, almost planar, aromatic compounds that show similar physical, chemical and biological

properties (Rappe, 1984). The number of chlorine atoms in these compounds can vary between one and eight, and a possibility of 75 PCDD and 135 PCDF positional isomers exist. The isomers with 4 to 6 chlorine atoms and all lateral (2,3,7,8) positions substituted with chlorine exhibit the highest activity and acute toxicity (Rappe, 1984). The chemical structures of PCDDs, PCDFs and 2,4,5-T are shown in Appendix 1.

2.0 METHODS

2.1 Site Description

A site was selected in northern New Brunswick (Figure 1) which was scheduled to receive a 2,4,5-T treatment as part of a MNR conifer release program. The site was located in the headwaters area of the Jacquet River ($47^{o}44'$ N and $66^{o}25'$ W) and was approximately 202 hectares in size.

Within the spray block was located a small marshy pond (an old beaver dam) which was fringed by a 30 metre band of 20 metres high white spruce (Picea glauca). The pond was drained by a stream which had a very low and variable flow rate (i.e. 4-12 L/min). The watercourse and its margins covered an area of approximately 15 ha within the block and normally would have been excluded from spray, however, arrangements were made to treat the pond and lower areas of the watercourse.

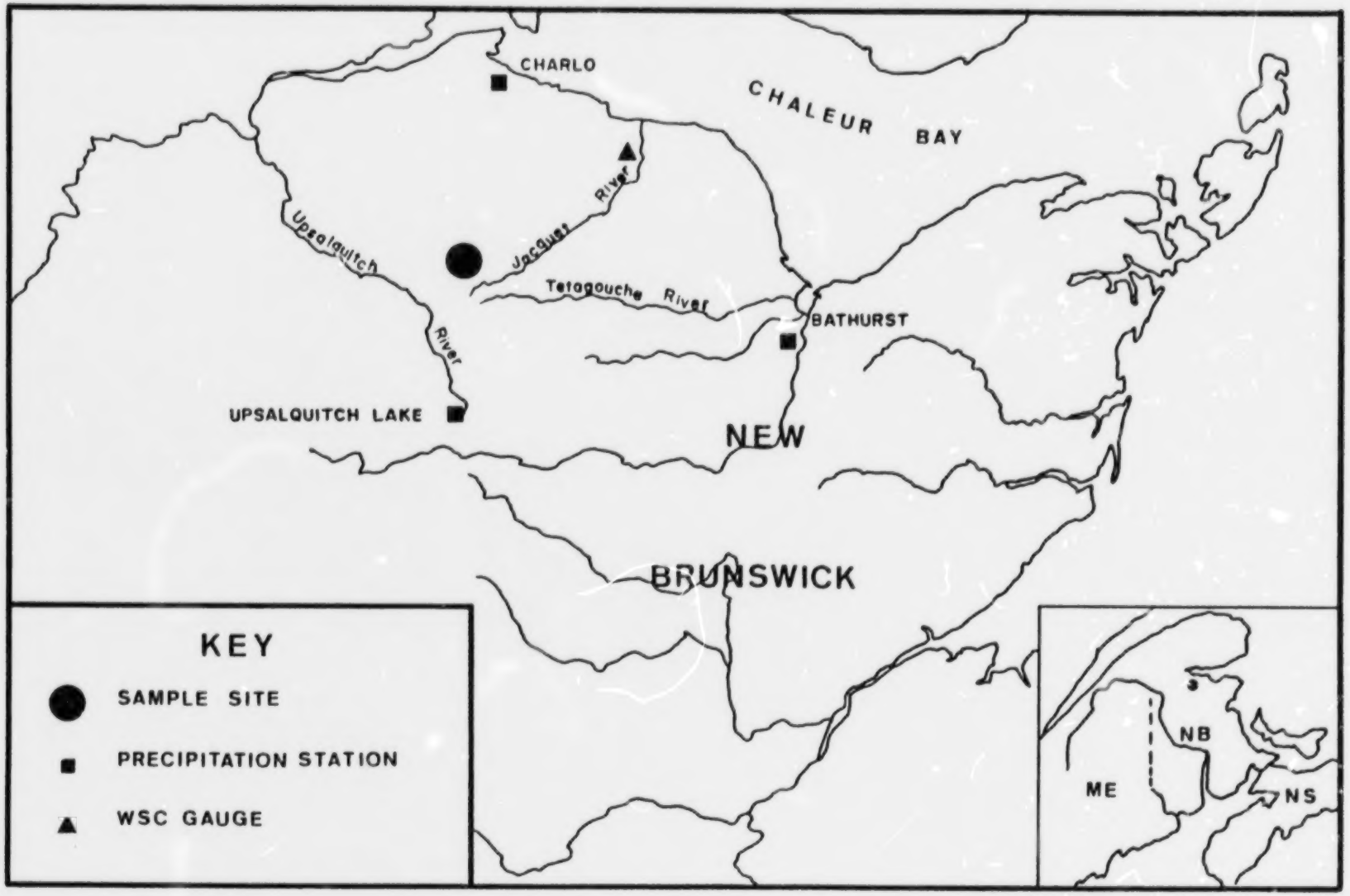


FIGURE 1 - SAMPLING AREA

2.2 Herbicide Application

Spray application over the lower portion of the block took place on September 3, 1984, using a Hughes 300 helicopter equipped with boom and nozzles (Tee Jet D89/45). Boom pressure was 27 psi and air speed was 105 km/hr. The upper portion of the block (pond) was sprayed in the same day with a Bell 206 helicopter equipped with boom and nozzle (Tee Jet D8-D10). Boom pressure was 10 psi and flight speed was 130 km/hr.

Droplet size with this technology is expected to range from 200-400 um (manufacturers specification). Both helicopters were calibrated to deliver 1.68 kg of active ingredient in 37.4 litres of total formulation per hectare. Brush-Rhap emulsifiable concentrate formulation was used.

2.3 Sampling Program

The program included sampling 4 days prior to spray followed by 3-, 12-, 37-, and 86 hours post-spray sampling. The pre-spray sampling was performed on August 30 and the first post-spray sampling on September 3.

2.4 Sampling Procedures

2.4.1 Samples for herbicide and physical-chemical analyses

All sample bottles were chosen and pre-washed according to the parameters to be analyzed (WQB, 1983). Water sampling for 2,4,5-T and physical-chemical parameters was done by hand. Sample bottles were

immersed so that the mouth was approximately 1 cm below the water surface. Water samples for physical and chemical analyses were preserved in the field using standard WQB procedures (WQB, 1983). Water samples for herbicide content analyses were kept in coolers in the field. On their arrival at the Moncton laboratory, they were refrigerated at $4^{o}C$, and extracted the following day. The study required triplicate water samples for phenoxy herbicide analyses, duplicate water samples for the physical-chemical analyses, and duplicate bottom sediment samples for 2,4,5-T analyses.

Bottom sediment samples were collected using a 15 x 15 cm Ekman dredge. The dredge was allowed to settle slowly in the sediment and then triggered to close with a messenger. Once collected, the sediment sample was carefully released from the sampler into a clean Pyrex tray and subsequently sub-sampled by taking approximately the top 3.0-4.0 cm with an aluminum scoop. Two sub-samples were taken from each grab and placed in a pre-washed aluminum tray, frozen within 4 hours of sampling and sent to the WQB laboratory in Moncton, for analyses. The procedure of removing two sub-samples from each grab was followed due to the difficulty in obtaining good sediment samples.

2.4.2 Samples for PCDD and PCDF analyses

Brook trout (Salvelinus fontinalis) which had been electrosiened from an adjacent brook or obtained from a local fish rearer (Girous Enterprises, Charlo, New Brunswick), were held in live cages in the pond, approximately six fish in each cage. Cages consisted of a wooden frame (75 cm x 50 cm x 50 cm) over which a polypropylene

mesh was placed. Prior to spray and at various times after spray (3, 12, 37 and 86 hours) a composite sample of four fish were removed. Fish were removed from the cages by hand, killed by cervical dislocation, wrapped in aluminum foil which had previously been rinsed with pesticide grade hexanes and placed in airtight plastic bags. Samples were frozen immediately and maintained at -20°C until analysis. Whole fish were homogenized and sub-sampled for analysis.

Cores of the pond sediments were obtained at the same time intervals as described above. Teflon core tubes (Extran 300, 35 mm I.D.) which had previously been detergent washed, rinsed with deionized water, and rinsed with pesticide grade hexanes, were pushed by hand into the pond sediment as far as possible. The bottom of the core tube was then sealed by sliding one hand down the length of the tube and placing several fingers over the open end. The core tube was then withdrawn, PVC caps placed over the ends and the caps sealed with electrical tape. The cores were immediately frozen and stored at -20°C until analysis. At the time of analysis, the top 5 cm (measured from the water/sediment interface) was removed and analyzed.

Aquatic bryophytes (Fontinalis antipyretica) were sampled by hand at the times indicated above. Plants were placed in 500 mL mason jars which had been previously detergent washed, deionized water and hexanes rinsed. Hexanes rinsed aluminum foil was used to cover the jar before the top was replaced. Samples were immediately frozen and stored at -20°C until analyzed.

Soil samples from within the target area were taken prior to spray

and at 14, 37 and 86 hours after spray. The organic layers at sample sites were collected using a hexanes-rinsed stainless steel scoop. The sampling scoop was rinsed with hexanes between samples and an attempt was made to minimize the amount of mineral soil which was taken with each sample. Soil was placed in 500 mL mason jars which had been cleaned in the same manner as above. Samples were frozen and stored at -20°C until analyzed.

2.5 Analytical Procedures

All laboratory analytical methodologies used for herbicide and water physical-chemical analyses are found in the Analytical Methods Manual of the WQB (1979). A listing of the parameters studied and the corresponding NAQUADAT parameter numbers is given in Appendix 2. These samples were done by the WQB laboratory in Moncton.

All PCDD and PCDF analyses were done under contract by the Brehm Laboratory, Wright State University, Dayton, Ohio. A detailed description of the general procedures used for these determinations is presented in Appendix 3. Samples which required digestion prior to extraction were handled in the following way. Whole fish were homogenized in a blender and an aliquot of the homogenized sample spiked with the appropriate internal standards and digested using concentrated hydrochloric acid. The aquatic moss samples were spiked with the radio-labelled internal standards and then digested using concentrated hydrochloric acid. Soil and sediment samples were spiked and extracted in a Soxhlet extractor using benzene as the extraction solvent. Only the top 5 cm of each core sample was analyzed.

Initially, only a limited number post-spray samples were analyzed. When positive values were obtained for some of these samples (aquatic moss) additional post spray and pre-spray samples, for that matrix, were analyzed.

3.0 RESULTS AND DISCUSSION

3.1 Water Characteristics of the Pond

The physical parameters and major ions data are displayed in Table 1. The nutrients and metals data are displayed in Tables 2 and 3. The data in Tables 1, 2 and 3 show that changes occurred in the pond's water chemistry with time (from pre-spray to 86 hours post-spray). It seems that as water flowed out of the pond it was replaced by new water with some different physical-chemical characteristics (see figures 2 and 3). Colour, specific conductance, total alkalinity, calcium, magnesium, dissolved organic carbon, iron, manganese and zinc values all increased in the water during the study. It would seem that runoff dominated water chemistry changed to baseflow groundwater chemistry.

According to available geological mapping for the area, the soil is mainly composed of shale and limestone with minor volcanic and intrusive rocks. Also found are ferrugenous and manganiferous chert and argillite. The changes in water chemistry seem related to this geology as alkalinity, manganese, iron, calcium, magnesium and zinc concentrations increase with time while sulphate concentration decreases.

TABLE 1. Physical parameters results and major ions in the water

Parameter	Pre-spray		3 hrs post		12 hrs post		37 hrs post		80 hrs post	
Colour apparent, relative units	45	40	50	60	50	50	50	50	60	60
Specific Conductance, USIE/cm	36	36	41	41	41	41	43	43	46	46
Turbidity, JTU	1.9	2.4	3.2	3.6	1.9	1.9	2.3	2.1	2.1	2.7
Alkalinity total, mg/L $CaCO_3$	13.9	13.8	16.5	16.2	17.0	17.2	18.0	17.9	20.4	20.1
pH, pH units	6.4	6.4	6.4	6.4	6.3	6.4	6.3	6.3	6.4	6.4
Calcium, diss., mg/L Ca	4.8	4.8	6.1	6.1	6.1	6.1	6.3	6.3	6.7	7.0
Magnesium, diss., mg/L Mg	0.40	0.40	0.45	0.45	0.50	0.50	0.50	0.50	0.54	0.52
Potassium, diss., mg/L K	0.4	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.5
Sodium, diss., mg/L Na	2.0	1.9	2.0	2.0	2.0	2.0	2.0	2.0	2.1	2.1
Chloride, diss., mg/L Cl	0.8	0.8	0.8	0.9	0.7	0.8	0.8	0.8	0.9	1.0
Sulfate, diss. (I.C.), mg/L SO_4	0.8	0.8	0.8	0.7	0.7	0.7	0.6	0.7	0.5	L0.5
D.I.C., mg/L C	3.7	3.7	4.6	4.5	4.8	4.4	5.1	5.4	5.6	6.3
Dissolved oxygen (field) mg/L O_2	12.0		8.0		5.0		4.5		4.0	

TABLE 2. Nutrients in the water

Parameter	Pre-spray		3 hrs post		12 hrs post		37 hrs post		86 hrs post	
Silica reactive, mg/L SiO_2	9.7	9.4	10	10	10	9.9	9.3	9.3	9.7	9.9
D.O.C., mg/L C	4.9	5.4	6.0	5.7	5.7	5.4	6.0	6.2	7.4	6.1
Nitrogen total, mg/L N	0.30	0.21	0.29	0.27	0.26	0.24	0.22	0.18	0.34	0.35
Nitrite-Nitrate, mg/L N	0.17	0.11	0.15	0.15	0.14	0.14	0.08	0.06	0.14	0.07
Phosphorus total, mg/L P	0.020	0.021	0.050	0.032	0.023	0.031	0.31	0.20	0.031	0.031

TABLE 3. Selected metals in the water

Parameter	Pre-spray		3 hrs post		12 hrs post		37 hrs post		86 hrs post	
Iron, ext., mg/L Fe	0.50	0.40	0.55	0.61	0.54	0.47	0.51	0.56	0.69	0.72
Manganese, ext., mg/L Mn	0.09	0.07	0.08	0.09	0.14	0.12	0.16	0.18	0.33	0.33
Copper, ext., mg/L Cu	L0.002	L0.002	L0.002	L0.002	L0.002	L0.002	L0.002	L0.002	L0.002	L0.002
Zinc, ext., mg/L Zn	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	L0.01	0.03	0.04
Cadmium, ext., mg/L Cd	L0.001	L0.001	L0.001	L0.001	L0.001	L0.001	L0.001	L0.001	L0.001	L0.001
Lead, ext., mg/L Pb	0.002	0.002	L0.002	0.002	0.002	0.002	0.002	L0.002	L0.002	0.002
Aluminum, ext., mg/L Al	0.080	0.070	0.080	0.085	0.095	0.080	0.070	0.080	0.080	0.080

FIG.2-VARIATION OF WATER CHEMISTRY WITH TIME

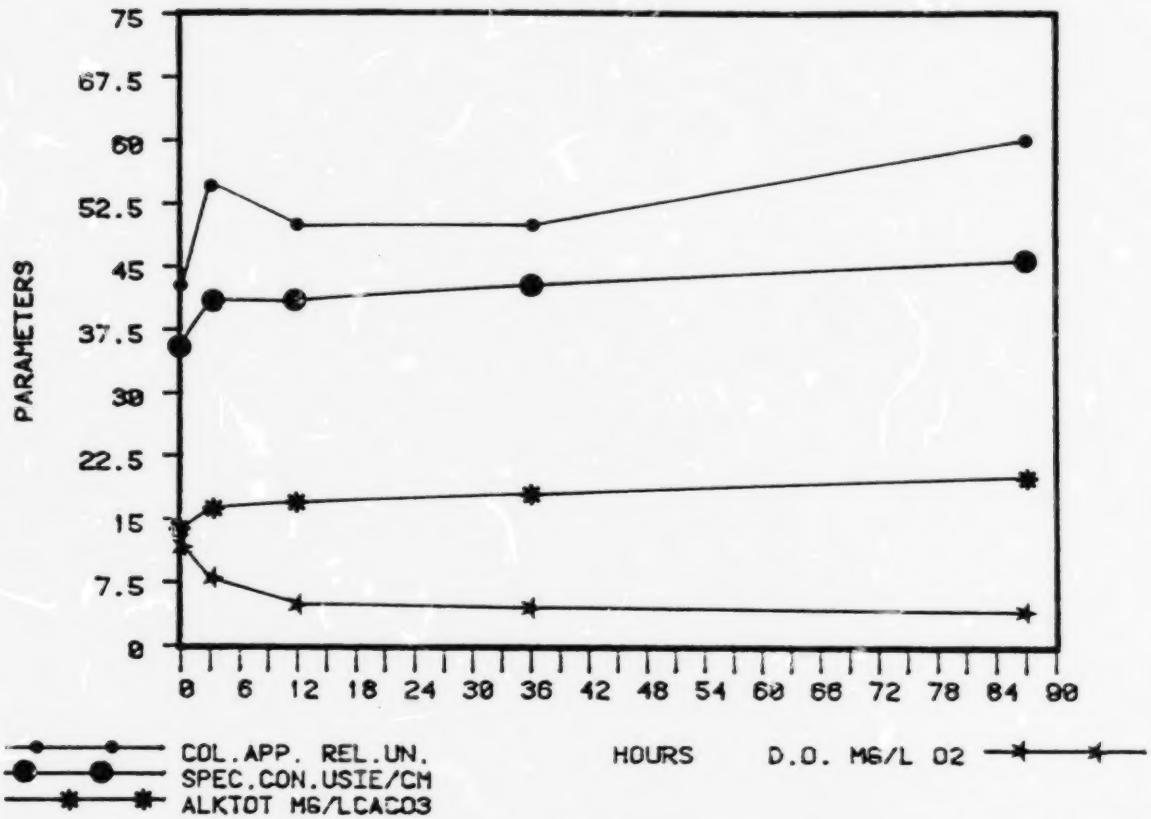
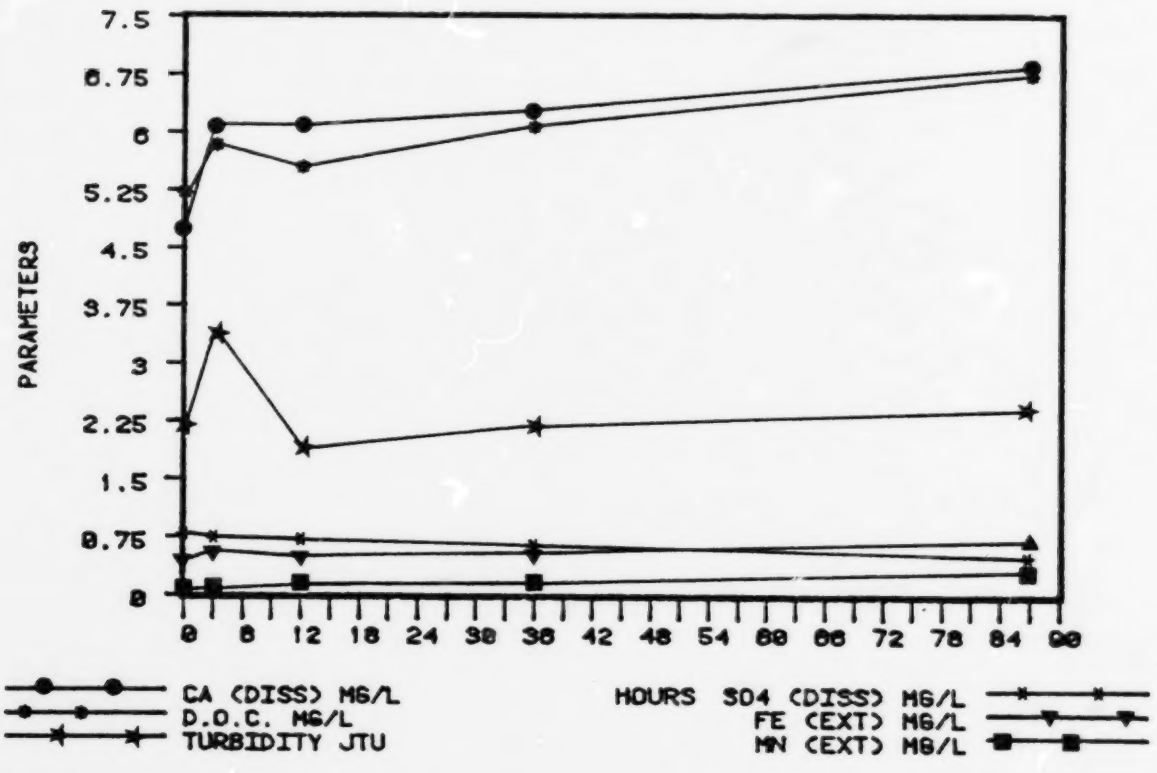


FIG.3-VARIATION OF WATER CHEMISTRY WITH TIME



For the period of interest in this study, data from the WRB gauging station located near the mouth of the Jacquet River are available. Also wet precipitation data from the Charlo CANSAP station, 30 km north of the study site, from Lake Upsalquitch station, 30 km south of the site, and from Belledune station, 55 km northeast of the site are available. The data from these stations, for the period of interest, are shown in Table 4 (see also figures 4 and 5).

Since the sampling site is located in the headwaters area of the Jacquet River, it is reasonable to assume that any rain events recorded at the Charlo, Upsalquitch Lake and Belledune stations on the same date could affect it. This assumption would be reinforced if the discharge of the Jacquet River peaks on or near the event date, since there would be a lag in response at the WRB station.

The rain values from the Charlo, Upsalquitch Lake and Belledune stations and the daily mean discharge values from the Jacquet River gauging station show that there were precipitation events just before and after the pre-spray sampling done on August 30, and that no precipitation occurred during the post-spray sampling period of September 3 to 7. This could mean that at the beginning of the study (pre-spray), the pond's water was runoff dominated and that during the dry period of September 3 to 7, the pond gradually reached baseflow groundwater. This is in accordance with the geology of the area and the water chemistry observed. Also, because the pond is small and shallow, it is possible to observe rapid changes in the water chemistry.

Field D.O. values (Table 1) in the pond water decreased during the

TABLE 4. Daily mean discharge values for the Jacquet River and rain values from the 3 nearest precipitation stations for the period of August 25 to September 9, 1983

Date	Jacquet River WRB Station	Charlo CANSAP Station	Upsalquitch Lake Station	Belledune Station	Remarks
	m^3/s	mm	mm	mm	
25-08-83	1.67	-	-	-	
26-08-83	1.61	TR	1.4	0.6	
27-08-83	1.62	2.8	1.8	0.4	
28-08-83	1.59	0.2	6.2	0.7	
29-08-83	1.72	TR	3.0	0.5	
30-08-83	1.59	TR	-	-	pre-spray sampling(evening)
31-08-83	1.60	4.7	7.0	8.3	
01-09-83	1.92	1.5	8.0	-	
02-09-83	1.84	3.8	3.2	2.1	
03-09-83	1.77	-	-	-	post-spray sampling(")
04-09-83	1.58	-	-	-	" " " (morning)
05-09-83	1.48	-	-	-	" " " "
06-09-83	1.39	-	-	-	
07-09-83	1.33	10.6	10.2	5.7	" " " "
08-09-83	1.53	-	-	-	
09-09-83	1.50	9.9	20.2	12.6	

TR: Traces
- : No precipitation

FIG.4-HYDROGRAPH OF JACQUET RIVER

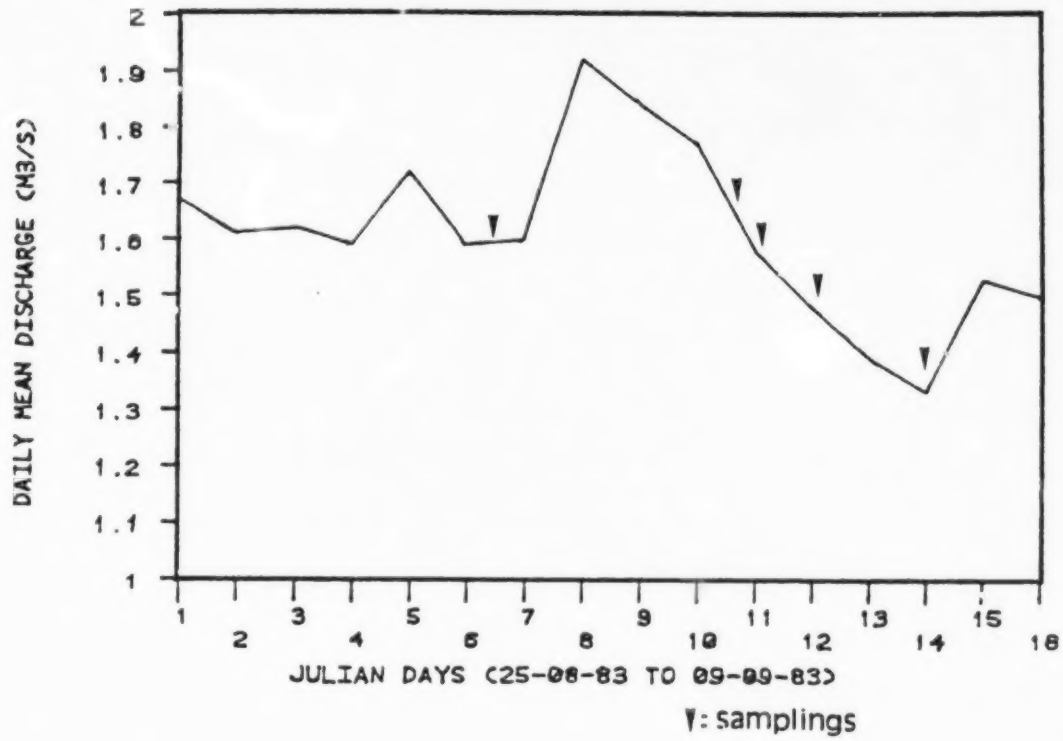
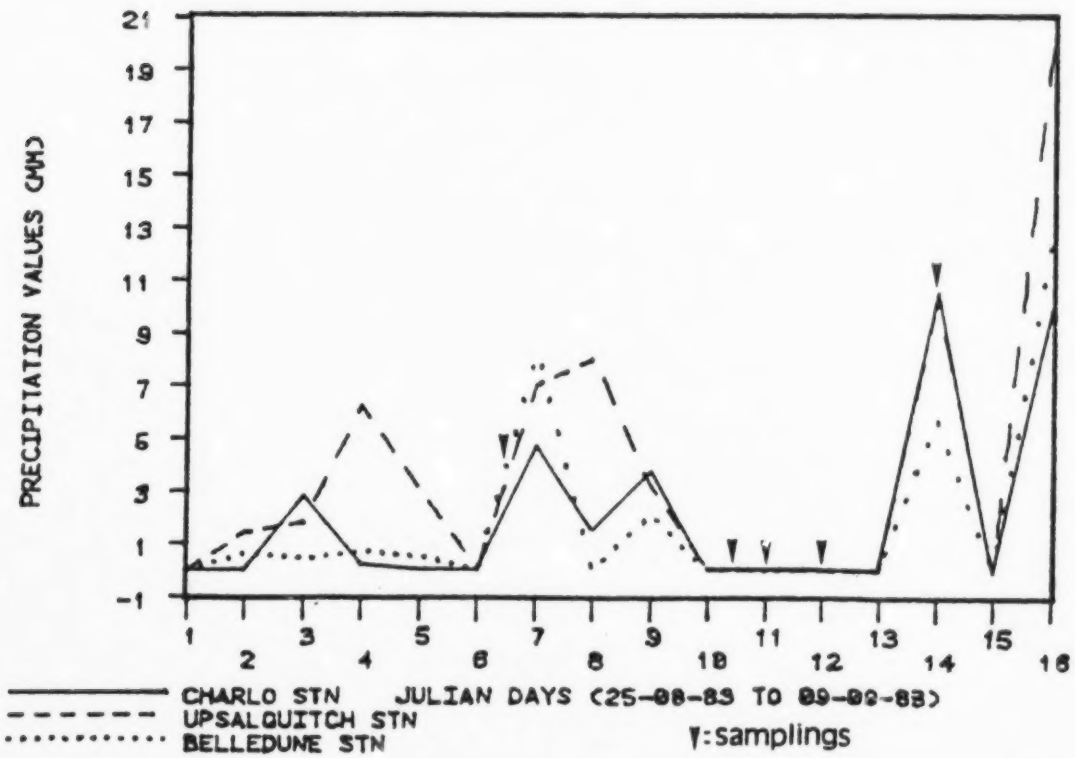


FIG.5-PRECIPITATION DATA



study. This is another indication that a possible change to groundwater occurred. The lower D.O. values found with time could also be partly related to the effects of the herbicide treatment on primary production in the pond. However, from this study, no relation can be made between physical-chemical and biological changes in the water due to herbicide treatment.

3.2 Herbicides in Water and Bottom Sediment Samples

Results of herbicide analyses in water and sediment samples are presented in Table 5. These results must be viewed with care because in some cases a large variability within sequential triplicate water samples was observed. These data show that concentrations of 2,4,5-T isooctyl ester and 2,4,5-T in water of the pond decreased with time.

Hydrolysis of ester formulations of phenoxy herbicides has been shown to be an important breakdown process, and it is controlled by pH (Norris, 1981). The corresponding and generally less toxic phenoxy acids are mainly degraded microbiologically (NRCC, 1978). Bailey et al. (1970) have reported rapid hydrolyses (50% in 5-8 hours) of some esters of fenoprop (2,4,5-trichlorophenoxypropionic acid) in treated ponds. Zepp et al. (1975) have shown that hydrolyses of 2,4-D esters were more rapid in alkaline waters: hydrolytic half lives of few hours at pH 9.0 compare to up to 1500 days at pH 6.0.

Figure 6 illustrates the variations of 2,4,5-T isooctyl ester and 2,4,5-T concentrations in water during the post-spray period, using median molar concentration values. These limited results suggest that

TABLE 5. Concentration of 2,4,5-T isooctyl ester in water and 2,4,5-T in water and sediment samples

	Water		Sediment
	2,4,5-T isooctyl ester, ug/L	2,4,5-T ug/L	2,4,5-T mg/kg
Pre-spray	L0.01	L0.01	L0.002
	L0.01	L0.01	L0.002
	L0.01	L0.01	-
3 hrs Post-spray	49.	21.	0.30
	83.	51.	0.29
	13.	29.	-
12 hrs Post-spray	44.	26.	0.035
	52.	35.	0.016
	25.	30.	-
37 hrs Post-spray	9.7	15.	0.039
	10.	19.	0.11
	7.2	16.	-
86 hrs Post-spray	5.1	6.4	0.064
	4.2	12.	0.020
	3.4	8.7	-

L: lower than detection limit

hydrolysis of the ester occurred, which would explain the higher acid concentration in the second sample and the corresponding lower ester concentration observed then, compared to the levels in the previous sample (9 hours before). Subsequent to this, the steeper slope of the ester curve indicates that it is still being removed by hydrolysis as well as by other pathways whereas the acid concentration is being augmented by the hydrolysis reaction but diminished by dilution and degradation. This study did not however, evaluate any of the possible microbiological or photochemical degradative processes.

In the bottom sediments of the pond, the highest 2,4,5-T concentration was observed in samples collected soon after treatment (3 hours post-spray) (Figure 7). Contamination of that first sample is possible. Rapid microbial degradation at the surface of the pond bottom sediment is also a possibility to explain the lower levels observed in following samples. However, samples collected at 12 hours post-spray presented lower values than the samples taken 25 hours later or even 74 hours later, which seem to indicate that if microbial activity accounted for the rapid decrease in concentration between the 3 hours and 12 hours post-spray samples, it ceased to function after 12 hours. Previous work (Anonymous, 1973) has shown that 2,4,5-T degrades in 2 to 3 months in submerged clay soils. Kries (1947) and Brown and Mitchell (1948) recognized that 2,4-D was rapidly inactivated by microbial activity in moist soil. DeRose and Newman (1947) found that 2,4,5-T persisted longer in moist soil (93 days) after application than 2,4-D. Assuming similar behaviour in bottom sediment, in addition to results observed in this study, it is suggested that continuation of bottom sediment sampling over a longer period would have been necessary to determine the

FIG.6- VARIATION OF 2,4,5-T AND
2,4,5-T ISOOCTYLESTER IN WATER

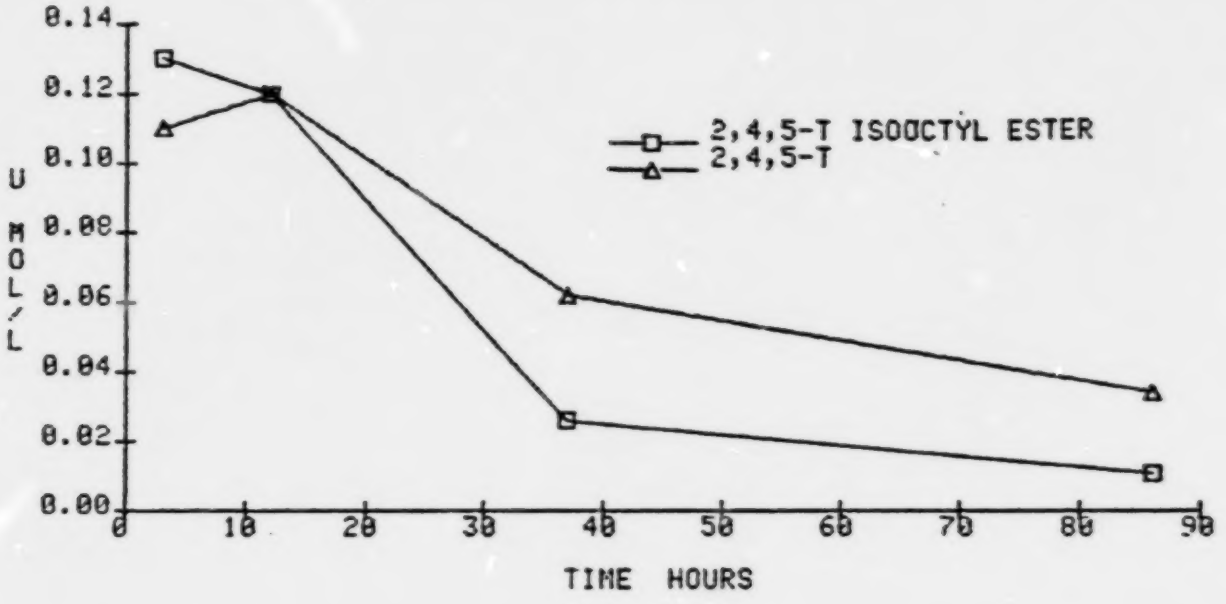
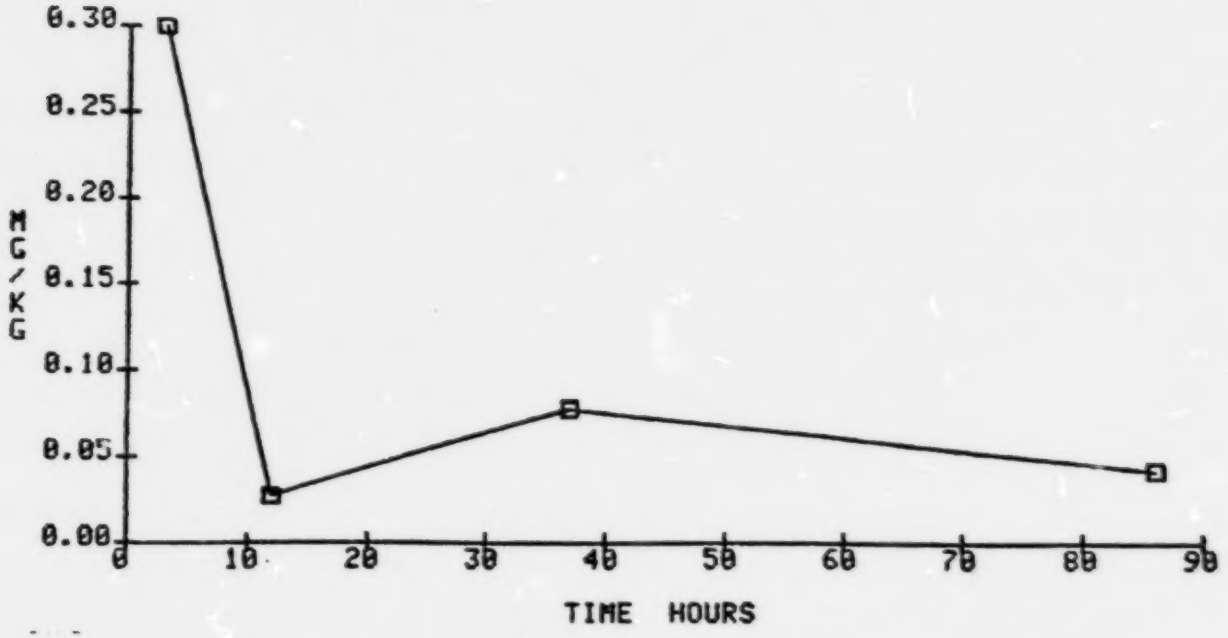


FIG.7- VARIATION OF 2,4,5-T IN BOTTOM SEDIMENTS



length of time that detectable 2,4,5-T levels persisted in that milieu.

The large variability observed between some of the duplicate sediment samples (Table 5) could be explained by the fact that, previous to duplicate sub-samplings, the sediment grab samples were not mixed.

3.3 PCDDs and PCDFs in the Technical Product and Environmental Samples

The results of PCDD and PCDF analyses in formulation samples (technical product) are contained in Table 6. No di- or tri- CDDs or di- or tri- CDFs were detected in these analyses and the minimum detectable concentrations were in the range of 1.0 to 3.0 parts per billion (ppb). Both tetra- CDD and tetra- CDF were detected in the samples analyzed. High resolution gas chromatograph/mass spectrometer analysis indicated that the tetra- CDD detected consisted entirely of 2,3,7,8. The tetra- CDF detected was not the 2,3,7,8-TCDF but it could not be positively identified. The technical product also contained the hexa- CDFs, hexa- CDDs, hepta- CDDs and octa- CDD. Due to lack of appropriate reference standards none of these isomers could be positively identified.

Most of the environmental samples had no measurable quantities of CDFs and CDDs (Appendix 4 and 5). The detection limits for these analyses ranged from 2.0 to 100 ppt.

The only positive results reported were for CDF analysis of aquatic moss samples (Table 7). No penta-, hexa-, hepta- or octa- CDFs were detected. The di-, tri- and tetra- CDFs were detected in both pre and

post spray samples, however, the highest concentrations were reported for samples collected at 3 hours after the spray event. The highest concentrations of CDF was the tetra- group of congeners which occurred at 3 hours after spray.

The mean total concentrations of PCDD and PCDF (36 ppb and 22.4 ppb) respectively in the technical product are somewhat low, compared with the values reported in the literature (Rappe et al., 1978; Norstrom et al., 1979; Ahling et al., 1977). The tetra congener, which consisted entirely of the 2,3,7,8 isomer is lower than levels of this isomer found in older 2,4,5-T formulations (Rappe et al., 1978) and well within the existing Agriculture Canada regulations of 100 ppb.

The high values, reported for the more chlorinated CDD congeners (hepta- and octa-) relative to the 2,3,7,8 tetra congener are somewhat surprising and to the best of our knowledge have never previously been reported. The values reported for these congeners are well above detection limits, however, and the contractor is confident in reporting these results.

Tetra- and penta- CDFs have previously been reported as contaminants of 2,4,5-T (Norstrom et al., 1979; Rappe et al., 1978), however, contamination by the hexa congener has not previously been reported. These authors have also noted that tetra-CDF is usually in approximately the same proportion as the tetra-CDD. Our results indicate an order of magnitude greater CDF than CDD contamination. It should be stated, however, that while samples of

TABLE 6 RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS FROM HERBICIDE SAMPLES
(Concentrations of Total CDDs/CDFs in nanograms/g or ppb with minimum detectable concentrations in parenthesis)

SAMPLE TYPE	CDDs						
	di-	tri-	tetra-	penta-	hexa-	hepta-	octa-
Herbicide From Drum	ND (2.0)	ND (1.5)	1.1	ND (3.0)	ND (10)	13	16
Herbicide From Drum	ND (1.0)	ND (1.0)	1.2	ND (1.5)	13	13	15

SAMPLE TYPE	CDFs						
	di-	tri-	tetra-	penta-	hexa-	hepta-	octa-
Herbicide From Drum	ND (3.0)	ND (1.0)	12	ND (5.0)	7.8	ND (6.0)	ND (3.0)
Herbicide From Drum	ND (3.0)	ND (1.5)	15	3.5	6.5	ND (5.0)	ND (3.0)

SAMPLE TYPE	RECOVERY OF INTERNAL STANDARD		
	2,3,7,8-TCDD	1,2,3,4,6 + 8-HpCDD	-OCDD
Herbicide From Drum	51%	35%	50%
Herbicide From Drum	82%	90%	78%

TABLE 7 RESULTS OF AQUATIC MOSS ANALYSIS FOR CDFs
(Concentrations of CDFs expressed in picograms/g or ppt with minimum detectable concentrations in parenthesis)

SAMPLE TIME RELATIVE TO SPRAY	CDDs						
	di-	tri-	tetra-	penta-	hexa-	hepta-	octa-
Pre Spray	106	145	130	ND (2.1)	ND (3.1)	ND (2.9)	ND (11)
Pre Spray	ND (38)	56.1	47.3	ND (3.9)	ND (5.5)	ND (5.4)	ND (28)
3 hr Post	ND (25)	40	60	ND (10)	ND (20)	ND (20)	ND (20)
3 hr Post	200	800	1000	ND (80)	ND (25)	ND (20)	ND (25)
37 hr Post	ND (14)	ND (4.8)	ND (2.3)	ND (3.4)	ND (3.1)	ND (2.0)	ND (45)
37 hr Post	ND (17)	ND (10)	ND (3.1)	ND (4.7)	ND (5.5)	ND (2.2)	ND (3.4)
86 hr Post	ND (80)	150	300	ND (15)	ND (20)	ND (20)	ND (20)
86 hr Post	ND (30)	40	70	ND (10)	ND (20)	ND (15)	ND (20)
86 hr Post	ND (59)	14	143	ND (11)	ND (3.5)	ND (2.4)	ND (26)

ND indicates not detected.

technical product were stored in ultra clean glass containers, they were taken from the drums by means of a polyethylene siphon hose and this brief contact may have resulted in contamination by interfering chemicals.

The observation of CDF residues in the aquatic moss samples is not entirely surprising since this genus has been demonstrated to accumulate anthropogenic chemicals such as forestry pesticide (Eidt et al., 1984). It is unlikely, however, that the source of the CDF in moss samples was the CDF contamination of the herbicide used in 1983 since some pre-spray samples contained measurable amounts and the tri- and di-congeners predominate in the moss while the higher chlorinated congeners predominate in the pesticide formulation. It is unlikely, as well, that the contamination of moss is due to long-distance transport of CDF from combustion sources since it has recently been demonstrated that environmental samples which are contaminated by such sources contain predominantly octa CDF congeners (Czuczwa et al., 1984). These authors have also definitively established that CDF is not generated during forest fires. The CDF congener ratios in the moss samples are more comparable to the congener ratios normally observed in commercially available 2,4,5-T (P. Barrett, pers. comm.). There was an application of 2,4,5-T to an approximate 200 hectare site located 2.5 kilometers distant from the site two years prior to sampling (B. Speer, pers. comm.) and the herbicide used in that operation may have had more "usual" congener ratios.

While the source of the CDF in the moss cannot be established, it is worth noting that tetra- CDF which predominated in moss samples is

one of the most toxic congeners (Rappe, 1984). It is impossible to say, on the basis of such limited sampling whether exposure to non-target herbivores is sufficient to cause toxicological problems.

4.0 SUMMARY

The results of this preliminary study suggest that hydrolysis of the isooctyl ester occurred in the pond. Dilution and loss by the exit stream explains the lower values of both ester and corresponding phenoxy acid observed with time. Results of 2,4,5-T in bottom sediment demonstrated a diminishing trend with time.

In the technical product samples, the tetra- CDD detected consisted entirely of 2,3,7,8. However the level of 2,3,7,8 isomer detected was lower than levels of this isomer observed in older 2,4,5-T formulations and much lower than the existing Agriculture Canada regulation of 100 ppb. Hexa- CDFs, hexa- CDDs, hepta- CDDs and octa- CDD were also detected in the technical product but were not positively identified.

Most of the environmental samples had no measurable levels of CDFs and CDDs, except for aquatic moss samples which contained some di-, tri- and tetra- CDFs in both pre and post samples, with the highest concentrations being detected in samples collected 3 hours after the spray event. It should be stated that detection of CDFs in aquatic moss samples is significant, however, on the basis of herbicide formulation analyses it cannot be stated that the 2,4,5-T used for spraying was the source of the contamination.

5.0 RECOMMENDATIONS

In view of the results obtained in this preliminary study, here are a number of recommendations for future studies:

- Selection of another site where changes in water chemistry and hydrology are less important should be made.

- In this study, samples for herbicide analyses were kept cool (4°C) in the dark prior to laboratory extraction. To prevent possible changes in herbicide content in sample bottles before they reach the laboratory, it is suggested that field extraction, as a means of preservation, should be performed daily on water samples.

- Sample spiking with appropriate standards could be performed in the field. Spiked samples could then be analyzed to check recovery.

- If possible the top 0.5 to 1.0 cm of top bottom sediment should be sampled instead of the 3.0 to 4.0 cm sampled in this study which corresponds to a "dilution" of samples.

- CDFs results observed in pre and post spray aquatic moss samples warrant further investigation.

- Sampling over a longer period of time should be done to evaluate the persistence of the herbicide.

- In Canada, it appears that 2,4,5-T use will be replaced by the recently registered product Roundup (Glyphosate). Future studies should concentrate on this or any other herbicide utilized in the region to replace 2,4,5-T.

ACKNOWLEDGEMENTS

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APPENDIX 1

Chemical structures of PCDDs, PCDFs and 2,4,5-T

APPENDIX 2

NAQUADAT parameter list

APPENDIX 3

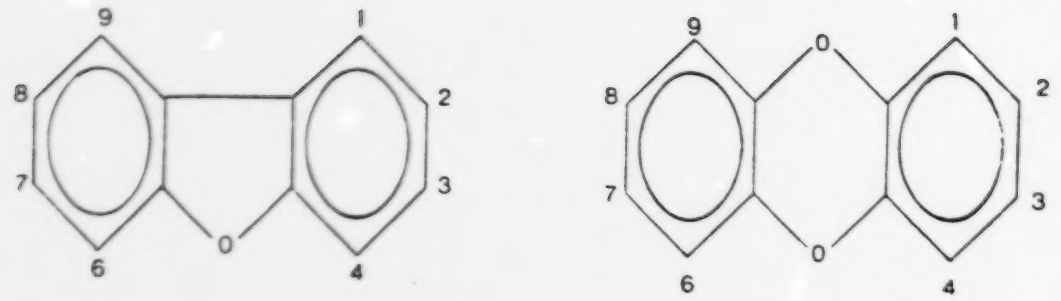
General description of Brehm laboratory methods

APPENDIX 4

Results of CDFs in environmental samples

APPENDIX 5

Results of CDDs in environmental samples

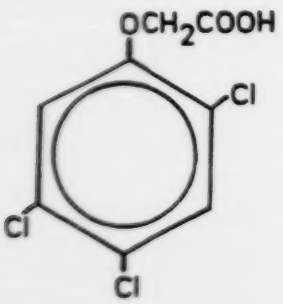


Ring structures of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs)

POSSIBLE NUMBER OF POSITIONAL PCDD AND PCDF ISOMERS*

CHLORINE SUBSTITUTION	NO. OF ISOMERS PCDDs	PCDFs
Mono-	2	4
Di-	10	16
Tri-	14	28
Tetra-	22	38
Penta-	14	28
Hexa-	10	16
Hepta-	2	4
Octa-	1	1
	75	135

*From Rappe and Buser 1980.



2,4,5-T

Appendix 2

Listing of the parameters analyzed and the corresponding NAQUADAT number

Parameter	NAQUADAT number
Colour apparent	02011L
Calcium, dissolved	20110L
Alkalinity, total	10101L
Iron, extractable	26304P
pH	10301L
Magnesium, dissolved	12102L
Potassium, dissolved	19103L
Sodium, dissolved	11103L
Specific Conductance	02041L
Chloride, dissolved	17205L
Silica reactive	14102L
Sulphate, dissolved (I.C.)	16309L
Carbon, dissolved, organic	06107L
Carbon, dissolved, inorganic	06154L
Nitrogen, total	07601L
Nitrogen, dissolved, NO2-NO3	07110L
Phosphorus, total	15413P
Manganese, extractable	25304P
Copper, extractable	29305P
Zinc, extractable	30304P
Cadmium, extractable	48302P
Lead, extractable	82302P
Aluminum, extractable	13305P
Turbidity	02073L
2,4,5-T Isooctyl ester	89452L
2,4,5-T (water)	18510L
2,4,5-T (sediment)	18511L

Brehm Laboratory, Wright State University, Dayton, Ohio 45435

Analytical Protocol for Analysis of Brush Rhap Formulations For Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans

A. Extraction of Sample and Preliminary Separation of CDDs and CDFs

1. Place an accurately weighed aliquot (typically 1.0 g of the sample in a 125 mL flint glass bottle (Teflon-lined screw cap). Add the appropriate quantity of internal standards, ($^{37}Cl_4$-2,3,7,8-TCDD, $^{37}Cl_4$-1,2,3,4,6,7,8-HpCDD, and $^{37}Cl_8$-OCDD or $^{13}C_{12}$-OCDD) to the sample.

2. Add 40 mL of hexane to the sample and agitate sample on a wrist action shaker for 60 minutes.

3. Extract the organic solution with 30 mL of 20% (w/v) potassium hydroxide by agitating for 10 minutes. Allow the mixture to stand for a period sufficient for complete separation of aqueous and organic layers and remove and discard aqueous base (bottom) layer into a base waste bottle.

4. Extract the organic solution with 30 mL doubly distilled water by agitating the sample for 10 minutes. Allow time for complete layer separation and discard the aqueous (bottom) layer.

5. Extract the organic solution with 30 mL of concentrated sulfuric acid by agitating the sample for 10 minutes. Allow time for complete layer separation and discard the acid (bottom) layer into acid waste bottle.

6. Repeat Step 5 until acid layer is colorless.

7. Extract the organic solution with 25 mL of doubly distilled water by agitating for 2 minutes. Allow for complete separation and remove aqueous (bottom) layer.

8. Dry the organic layer over anhydrous sodium sulfate and then quantitatively transfer the organic layer to a clean test tube and reduce the volume to incipient dryness using a stream of prepurified nitrogen while maintaining the test tube in a 55° water bath.

9. Fabricate a glass Macro-column (20 mm OD x 230 mm Long) tapered to 6 mm OD on one end. Pack the column with 1.0 g silica, 2.0 g silica containing 39% (w/w) 1 M NaOH, 1.0 g silica, 4.0 g silica containing 40% (w/w) sulfuric acid, and 2.0 g silica.

10. Quantitatively transfer the residue obtained in Step 8 to the column and elute the column with 90 mL hexane. Collect the eluent and concentrate to 1-2 mL in a centrifuge tube.

11. Construct a disposable liquid chromatography column as follows. Cut off a Pyrex 5 mL disposable pipet at the 2 mL mark and use the lower portion of the pipet. Pack the small end with a plug of silanized glass wool. Next add 1 gram of Woelm basic alumina previously activated overnight at 600°C in a muffle furnace and placed in a dessicator for 30 minutes just prior to use.

12. Using a disposable pipet, transfer the sample onto the liquid chromatography column.

13. Rinse the centrifuge tube with 2 consecutive 0.3 mL portions of hexane, and transfer the rinses to the alumina column.

14. Elute the column with 7 mL of 3% methylene chloride-in-hexane and discard the eluate (taking care not to let the column run dry).

15. Elute the column with 30 mL of 50% (v/v) CH_2Cl_2 in hexane and retain the eluate for analysis.

16. Concentrate the solution to approximately 1 mL, using a stream of pre-purified nitrogen as before. Rinse the centrifuge tube wall with an additional 1 mL of CH_2Cl_2 and reconcentrate.

17. Quantitatively transfer the residue (using methylene chloride) to a 2 mL micro-reaction vessel.

18. Evaporate the solution in the micro-reaction vessel almost to dryness as previously, rinse the walls of the vessel with approximately 0.5 mL CH_2CL_2, and evaporate contents just to dryness, storing extract in freezer until analysis.

19. Approximately 1 hour before GC-MS (GC-LRMS or GC-HRMS) analysis, dilute the residue in the micro-reaction vessel with 10 µl of tridecane. Gently swirl tridecane on cone portion of vessel to ensure dissolution of the dioxins. Withdraw an appropriate aliquot with a syringe and inject this sample into the GC-MS instrument.

B. Parameters for High Resolution Gas Chromatographic Low Resolution Mass Spectrometric (GC-LMRS) Analysis of the Extracts

Instrumentation: Perkin Elmer Sigma III Gas Chromatograph coupled through a custom-fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-50SM Data System.

Conditions for the Gas Chromatograph:

Column: 50M WCOT (DB-5) Silica Capillary

Carrier Gas: Hydrogen, 30 lb. head pressure

Column Temperature: Programmed. See Table 1 for details.

Interface Temperature: 250°C

Injector: Splitless Injection

Conditions for the Mass Spectrometer:

Selected Ion Monitoring Mode (for m/z's monitored and details of instrumental procedures see Tables 1 and 2

Ionizing Voltage: 70 eV

Accelerating Voltage: 4 KV

C. Reagents and Chemicals

The following is a listing of the reagents and chemicals utilized in the procedures outlined above. Potassium hydroxide, anhydrous sodium sulfate, and sulfuric acid were all Reagent Grade and were obtained from J.T. Baker Chemical Co. or Fisher Scientific Co., Fairlawn, N.J. Methanol, hexane, methylene chloride and benzene were "Distilled in Glass" quality obtained from Burdick and Jackson, Muskegon, Michigan. Woelm basic alumina (Activity Grade I) was obtained from ICN Pharmaceuticals, Cleveland, Ohio. Silica (Bio-Sil A) was obtained from Bio-Rad, Rockville Centre, New York. Doubly distilled water was obtained using the all-glass distillation apparatus in the Brehm Laboratory. Prepurified nitrogen was obtained from Airco, Inc., Montvale, New Jersey.

Reference standards utilized in these analyses and the sources of these are as follow:

2,7-dichlorodibenzo-p-dioxin, Analabs, Inc., North Haven, Conn.
1,2,4-trichlorodibenzo-p-dioxin, Analabs, Inc., North Haven, Conn.
All 22 tetrachlorodibenzo-p-dioxin isomers, prepared by Brehm Laboratory, Wright State University, Dayton, Ohio
$^{37}Cl_4$-2,3,7,8-tetrachlorodibenzo-p-dioxin, KOR Isotopes, Cambridge, Mass.
$^{13}C_{12}$-2,3,7,8-tetrachlorodibenzo-p-dioxin, Cambridge Isotopes, Cambridge, Mass.
1,2,3,7,8-pentachlorodibenzo-p-dioxin, KOR Isotopes, Cambridge, Mass.
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin, Dr. A. Poland, Univ. of Rochester, Rochester, N.Y.
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin, KOR Isotopes, Cambridge, Mass.
$^{37}Cl_4$-1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin, KOR Isotopes, Cambridge, Mass.
Octachlorodibenzo-p-dioxin, Analabs, Inc., North Haven, Conn.
$^{37}Cl_8$-octachlorodibenzo-p-dioxin, KOR Isotopes, Cambridge, Mass.
2,4-dichlorodibenzofuran, All CDFs obtained from U. S. FDA, Washington, D.C.
2,8-dichlorodibenzofuran
1,2,4-trichlorodibenzofuran
1,2,4,8-tetrachlorodibenzofuran
2,3,7,8-tetrachlorodibenzofuran
2,3,6,8-tetrachlorodibenzofuran
1,2,4,7,8-pentachlorodibenzofuran
1,2,4,6,7,9-hexachlorodibenzofuran
1,2,3,4,6,8,9-heptachlorodibenzofuran
Octaachlorodibenzofuran

D. Additional Details of Procedures Employed in Calibrating the GC-MS System In Conjunction With Quantitation of CDD/CDF

1. Criteria for GC/MS Identification of PCDDs/PCDFs

The criteria which GC-MS data must satisfy in order to be attributed to PCDDs/PCDFs present in the sample extracts are summarized below.

a. The mass chromatographic peaks produced by the unknown component must exhibit appropriate GC retention times; that is, they must fall within a retention time "window" established for a particular class of PCDD or PCDF (e.g. tetra-CDD). These "windows" are established by injecting representative standards for each class of PCDD and PCDF.

b. Mass chromatographic peaks produced by the component must exhibit the appropriate response for at least two major ions characteristic (that is, known to appear in the mass spectrum) of the particular PCDD or PCDF class being monitored. The ratio of relative intensities of the two ions monitored as indicators must correspond to that resulting from injection of a corresponding calibration standard within ± 30%.

c. In cases where the sample matrix causes shifts in the GC retention times of the components of interest, as compared to the retention times of the corresponding standards determined from a separate injection of standards, and as indicated by analogous shifts in the retention times for the internal standards added to the sample, the identification of a specific PCDD and/or PCDF must be confirmed by coinjection of the sample with an added quantity of the PCDD or PCDF isomer in question. Enhancement of a given mass chromatographic peak upon such coinjection leads to tentative assignment of the unknown peak as a specific PCDD or PCDF isomer.

2. Calibration of GC-MS and Quantitative Determination of PCDDs/PCDFs From GC-MS Data

There are 210 separate isomers of the PCDDs and PCDFs (75 PCDDs, 135 PCDFs), shown in Table 2. Since pure standards corresponding to all of these isomers are available in few if any laboratories, the approach currently utilized for calibration of the GC-MS instrumentation and quantitation of the compounds of interest in analyses such as those described here is to utilize selected standards representative of each chlorinated class of the PCDDs/PCDFs and to assume that the data obtained for these is representative of all isomers in each chlorinated group (for example, monochlorinated, dichlorinated, etc.). The procedures employed here entail, 1) obtaining a mass spectrum for each

of the representative isomers injected into the GC-MS, noting in particular the relative abundances of the m^+ and $(m+2)^+$ peaks (m indicates the molecular ion here); 2) determining gas chromatographic retention times for each isomer standard injected; and 3) based on the above data, select the ion masses appropriate for detecting and quantifying the isomers in the class of interest, and select the gas chromatographic retention time window appropriate for all isomers in the class (that is, the time interval during which the earliest-eluting and latest-eluting iscmers of a particular class elute from the gas chromatographic column and enter the mass spectrometer source-this must be estimated in cases where not all isomers of a given class are available). This retention time window must also include the retention time for the internal standard employed in quantifying the isomers of a particular class.

PCDDs/PCDFs in sample extract are quantified by obtaining the ratios of the mass spectral responses obtained for the ions characteristic of the native PCDDs/PCDFs to those of the appropriate internal standards (listed earlier in this section) added to the sample in known concentrations. The concentrations of the native PCDD/PCDF are then determined by comparing the above data with calibration curves, prepared by plotting the analytical results obtained for a series of standards, each of which contains a fixed concentration of internal standard, but varying concentrations of representative PCDD and/or PCDF. More specifically, the ratio of the ion intensity recorded for the native PCDD/PCDF to the ion intensity obtained for the appropriate labeled internal standard is plotted as a function of the ion intensity obtained for the labeled internal standard. Since the labeled internal standard is added at the beginning of the sample preparation/analysis scheme, and, since the internal standard is quantified at the same time as the native analyte(s), it is clear that the quantitative result obtained for the internal standard reflects the losses of PCDD/PCDF incurred during the course of sample handling and analysis.

TABLE 1

WRIGHT STATE UNIVERSITY, BREHM LABORATORY, DAYTON, OHIO 45435

SEQUENCE OF OPERATIONS IN GC-MS (MS-25) ANALYSES OF CHLORODIBENZODIOXINS AND CHLORODIBENZOFURANS IN SAMPLE EXTRACT

Elapsed Time (min)	Event	GC Column Temperature	Temperature Program Rate (°C/Min)	Ions Monitored By Mass Spectrometer (m/z)	Compounds Monitored
0.00	Injection, splitless	190°	--		
1.50	Turn on split valve	190°	--		
2.00	Begin temp. program to 220°C	190°C	5°C/min		
5.00	Open Column Flow to Mass Spec.	202°C	5°C/min		
6.50	Start PROGRAM #2				
	Sweep = 200 ppm	220°C	--	189.010	Cl_2 dioxins
	Time on Cl mass = 0.12 sec			235.980	Cl_2 furans
				237.977	Cl_2 furans
				251.974	Cl_2 dioxins
				253.972	Cl_2 dioxins
10.50	Stop PROGRAM #2	220°C	--		
11.00	Start PROGRAM #3	220°C	--	222.976	Cl_3 dioxins
	Sweep = 200 ppm			269.941	Cl_3 furans
	Time on Cl mass = 0.12 sec			271.938	Cl_3 furans
				285.935	Cl_3 dioxins
				287.932	Cl_3 dioxins
15.00	Stop PROGRAM #3	220°C	--		
15.50	Start	220°C	--	258.930	Cl_4 dioxins
				303.902	Cl_4 furans
				305.899	Cl_4 furans
				319.897	Cl_4 dioxins
				321.891	Cl_4 dioxins
				327.885	$^{37}Cl_4$ labelled TCDD
23.50	Stop PROGRAM #4	220°C	--		
24.00	Start PROGRAM #5	220°C	--	337.863	Cl_5 furans
	Sweep = 750 ppm			339.860	Cl_5 furans
	Time on penta mass = 0.2 sec			353.858	Cl_5 dioxins
				355.855	Cl_5 dioxins

Table 1 (cont.)

Elapsed Time	Event	GC Column Temperature	Temperature Program Rate (°C/Min)	Ion Monitored By Mass Spectrometer (m/z)	Compounds Monitored
25.00	Begin temp program to 230°C	220°C	5°C/Min		
34.50	Stop PROGRAM #5				
35.00	Start PROGRAM #6 Sweep = 150 ppm Time on each mass = .25 sec	230°C		373.821 375.818 389.816 391.813	Cl_4 furans Cl_4 furans Cl_4 dioxins Cl_4 dioxins
50.00	Begin temp program to 235°C		5°C/Min		
53.50	Stop PROGRAM #6	235°C	--		
54.00	Start PROGRAM #7 Sweep = 750 ppm Time on each mass = 0.35 sec	235°C	--	407.782 409.779 423.777 425.774 431.765	Cl_7 furans Cl_7 furans Cl_7 dioxins Cl_7 dioxins $^{37}Cl_4$ labelled HpCDF
70.00	Stop PROGRAM #7				
85.00	Start PROGRAM #8 Sweep = 750 ppm Time on each mass = 0.50 sec	235°C	--	441.732 443.740 457.738 459.735 471.717	Cl_8 furans Cl_8 dioxins Cl_8 dioxins Cl_8 dioxins $^{37}Cl_4$ labelled OCDD
95.00	Stop PROGRAM #8	235°C			
130.00	Return to initial temp.				

TABLE 2

WRIGHT STATE UNIVERSITY, BREHM LABORATORY, DAYTON, OHIO 45435

LIST OF ION MASSES MONITORED USING GC-SELECTED-ION MONITORING MASS SPECTROMETRY FOR SIMULTANEOUS DETERMINATION OF MONO-, Di-, TRI-, TETRA-, PENTA-, HEXA-, HEPTA-, and OCTA-, CHLORINATED DIBENZO-p-DIOXINS and DIBENZOFURANS

Class of Chlorinated Dibenzodioxin or Dibenzofuran	Number of Chlorine Substituents (X)	Monitored m/z for Dibenzofurans $C_{12}H_{8-x}OCl_x$	Monitored m/z for Dibenzo-p-dioxins $CH_{12}H_{8-x}O_2Cl_x$	Approximate Theoretical Ratio Expected on Basis of Isotopic Abundance
Mono	1	202.019[a]	218.013[a]	1.00
		204.016	220.011	0.35
Di	2	235.980[a]	251.974[a]	1.00
		237.977	253.972	0.69
Tri	3	269.941[a]	285.940[a]	0.99
		271.938	287.937	1.00
Tetra	4	303.902[a]	319.897[a]	0.74
		305.899	321.894	1.00
			327.885[b]	--
			[256.933	0.21
			258.930][c]	0.20
Penta	5	337.863[a]	353.858[a]	0.57
		339.860	355.855	1.00
Hexa	6	373.821	389.816	1.00
		375.818	391.813	0.87
Hepta	7	407.872	423.777	1.00
		409.779	425.774	1.00
			431.765	--
Octa	8	441.743	457.738	0.86
		443.740	459.735	1.00

a. Molecular ion peak. b. $^{37}Cl_4$-labelled standard peaks. c. Ions which can be monitored in TCDD analyses for confirmation purposes.

APPENDIX 4 RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF ENVIRONMENTAL SAMPLES FOR CDFs
(Concentrations of CDFs found in picograms/g or ppt with
minimum detectable concentrations in parenthesis)

SAMPLE TYPE	SAMPLING TIME	CDFs						
		di-	tri-	tetra-	penta-	hexa-	hepta-	octa-
Brook Trout*	3 hr Post	- (30)	- (25)	- (15)	- (15)	- (20)	- (25)	- (30)
Brook Trout	3 hr Post	- 150	- (40)	- (10)	- (30)	- (40)	- (20)	- (30)
Brook Trout	37 hr Post	- (30)	- (25)	- (10)	- (10)	- (15)	- (20)	- (30)
Brook Trout	37 hr Post	- (70)	- (80)	- (10)	- (15)	- (30)	- (20)	- (40)
Aquatic Moss	Pre Spray	106	145	130	- (2.1)	- (3.1)	- (2.9)	- (11)
Aquatic Moss	Pre Spray	- (38)	56.1	47.3	- (3.9)	- (5.5)	- (5.4)	- (28)
Aquatic Moss	3 hr Post	- (25)	40	60	- (10)	- (20)	- (20)	- (20)
Aquatic Moss	3 hr Post	200	800	1000	- (80)	- (25)	- (20)	- (25)
Aquatic Moss	37 hr Post	- (14)	- (4.8)	- (2.3)	- (3.4)	- (3.1)	- (2.0)	- (45)
Aquatic Moss	37 hr Post	- (17)	- (10)	- (3.1)	- (4.7)	- (5.5)	- (2.2)	34
Aquatic Moss	86 hr Post	- (80)	150	300	- (15)	- (20)	- (20)	- (20)

* This fish was dead when sampled.

Cont'd

APPENDIX 4 Cont'd RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF ENVIRONMENTAL SAMPLES FOR CDFs (Concentrations of CDFs found in picograms/g or ppt with minimum detectable concentrations in parenthesis)

SAMPLE TYPE	SAMPLING TIME	CDFs						
		di-	tri-	tetra-	penta-	hexa-	hepta-	octa-
Aquatic Moss	86 hr Post	- (30)	40 (25)	70 (15)	- (10)	- (20)	- (15)	- (20)
Aquatic Moss	86 hr Post	- (59)	14	143	- (11)	- (3.5)	- (2.4)	- (26)
Soil	14 hr Post	- (30)	- (20)	- (10)	- (10)	- (20)	- (20)	- (20)
Soil	14 hr Post	- (10)	- (10)	- (10)	- (12)	- (30)	- (20)	- (25)
Soil	86 hr Post	- (25)	- (30)	- (20)	- (10)	- (40)	- (15)	- (25)
Soil	86 hr Post	- (40)	- (40)	- (20)	- (25)	- (100)	- (20)	- (25)
Sediment	86 hr Post	- (20)	- (40)	- (10)	- (10)	- (50)	- (20)	- (20)
Sediment	37 hr Post	- (10)	- (15)	- (10)	- (15)	- (70)	- (20)	- (20)
Sediment	86 hr Post	- (15)	- (15)	- (10)	- (15)	- (30)	- (25)	- (20)
Sediment	37 hr Post	- (25)	- (30)	- (10)	- (15)	- (50)	- (20)	- (20)
Sediment	12 hr Post	- (40)	- (30)	- (10)	- (20)	- (40)	- (20)	- (20)
Sediment	12 hr Post	- (20)	- (25)	- (10)	- (25)	- (50)	- (20)	- (20)
Blank		- (10)		- (10)	- (10)	- (30)	- (20)	- (20)

APPENDIX 5 RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF ENVIRONMENTAL SAMPLES FOR CDDs
(Concentrations of CDDs found in picograms/g or ppt with
minimum detectable concentrations in parenthesis)

SAMPLE TYPE	SAMPLING TIME	CDDs							2,3,7,8	1,2,3,4,6,	
		di-	tri-	tetra-	penta-	hexa-	hepta-	octa-	TCDD	7,8 HpCDD	OCDD
Brook Trout*	3 hr Post	- (15)	- (30)	- (10)	- (60)	- (70)	- (25)	- (40)	79%	65%	58%
Brook Trout	3 hr Post	- (25)	- (100)	"	- (50)	- (40)	- (20)	- (30)	68%	80%	68%
Brook Trout	37 hr Post	- (50)	- (40)	"	- (30)	- (25)	- (20)	- (30)	75%	68%	55%
Brook Trout	37 hr Post	- (25)	- (80)	"	- (40)	- (30)	- (20)	- (40)	89%	81%	75%
Aquatic Moss	3 hr Post	- (15)	- (160)	"	- (20)	- (20)	- (15)	- (20)	79%	68%	68%
Aquatic Moss	3 hr Post	- (20)	- (25)	"	- (20)	- (20)	- (20)	- (20)	68%	80%	85%
Aquatic Moss	86 hr Post	- (10)	- (150)	"	- (20)	- (20)	- (20)	- (20)	70%	72%	85%
Aquatic Moss	86 hr Post	- (20)	- (20)	"	- (40)	- (30)	- (15)	- (20)	77%	85%	86%
Soil	14 hr Post	- (10)	- (40)	"	- (15)	- (30)	- (20)	- (20	68%	60%	58%
Soil	14 hr Post	- (10)	- (15)	"	- (10)	- (30)	- (20)	- (25)	71%	58%	64%

* This fish was dead when sampled.

Cont'd

APPENDIX 5 RESULTS OF HRGC-LRMS ANALYSES OF EXTRACTS OF ENVIRONMENTAL SAMPLES FOR CDDs
Cont'd (Concentrations of CDDs found in picograms/g or ppt with minimum detectable concentrations in parenthesis)

SAMPLE TYPE	SAMPLING TIME	CDDs									
		di-	tri-	tetra-	penta-	hexa-	hepta-	octa-	2,3,7,8 TCDD	1,2,3,4,6,7,8 HpCDD	OCDD
Soil	86 hr Post	- (10)	- (15)	- (10)	- (10)	- (40)	- (15)	- (50)	52%	43%	46%
Soil	86 hr Post	- (10)	- (50)	"	- (40)	- (100)	- (20)	- (40)	58%	85%	90%
Sediment	86 hr Post	- (20)	- (100)	"	- (10)	- (50)	- (20)	- (20)	96%	97%	99%
Sediment	37 hr Post	- (10)	- (40)	"	- (20)	- (70)	- (20)	- (20)	90%	100%	100%
Sediment	86 hr Post	- (15)	- (40)	"	- (15)	- (30)	- (25)	- (20)	88%	88%	95%
Sediment	32 hr Post	- (25)	- (80)	"	- (15)	- (50)	- (20)	- (20)	100%	100%	100%
Sediment	12 hr Post	- (40)	- (90)	"	- (20)	- (40)	- (20)	- (20)	79%	90%	85%
Sediment	12 hr Post	- (20)	- (90)	"	- (25)	- (50)	- (20)	- (20)	98%	100%	100%
Blank		- (10)		- (10)	- (10)	- (30)	- (20)	- (20)	82%	85%	85%